

Theory of Transport of Long Polymer Molecules through Carbon Nanotube Channels

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Abstract

A theory of transport of long chain polymer molecules through carbon nanotube (CNT) channels is developed using Fokker-Planck equation and direct molecular dynamics (MD) simulations. The mean transport or translocation time τ is found to depend on the chemical potential energy, entropy and diffusion coefficient. A power law dependence $\tau \sim N^2$ is found where N is number of monomers in a molecule. For 10^5 -unit long polyethylene molecules, τ is estimated to be $\sim 1\mu\text{s}$. The diffusion coefficient of long polymer molecules inside CNTs, like that of short ones, are found to be few orders of magnitude larger than in ordinary silicate based zeolite systems.

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Long chain polymer molecules and nanometer sized channels or pores present a unique complex nanosystem, where the size of molecules and channels are comparable and the interactions between them may dominate the relative configurations and transport dynamics. Nanochannels have been found in various solid state or biological systems and were subjects of previous studies, such as diffusions in microscopic zeolite channel [1], energies of polymer/molecule nanotube systems [2], and translocations of DNA through nanopores [3–5], for filtration, separation and sequencing applications, respectively. Carbon nanotubes (CNTs), formed by rolling graphene planes into tubular structures, provide structurally perfect and stable nanochannels, with variable size. The potential applications of CNT channels therefore could be many fold. The transport phenomena, such as translocation and diffusion, of long chain polymer molecules through CNT, however could be more complicated as compared with transport of small gas [7, 8] and water molecules [9] in CNTs due to the long length scale and entropy effects. The interaction between polymer molecules and CNTs and intra-polymer connectivities could also play significant role in the dynamics of such systems.

There are two processes in the transport of long chain polymer molecules to pass through CNT channels. First is the transport from surrounding solutions into CNTs, which we refer as translocation; second is the diffusion inside CNTs. In this letter the translocation of polymers into CNTs is studied using Fokker-Planck equation. An analytic expression for the mean translocation time τ is obtained, which is found to have a N^2 dependence on the number of monomers in the molecule. The calculated diffusion coefficient for linear polyethylene (PE) molecules, using molecule dynamics (MD) simulations, shows significant faster diffusion as compared with in silicate based zeolite systems. A fast translocation for very long chain polymer molecules through CNTs is also found.

When a polymer molecule goes inside a nanotube channel, the total energy E and entropy S will change due to the interactions with channel walls and geometric confinements. S is dependent on the conformation Ω of the molecule as $k_B \ln \Omega$, where $\Omega \sim N^{\xi-1} q_{eff}^N$ (N is the number of monomer units in the polymer molecule; q_{eff} is the effective coordination number for each unit; and ξ is an exponential parameter) [10]. Thus the entropy of a polymer molecule is $S = k_B(\xi - 1) \ln N + k_B N \ln q_{eff} + const.$ In a general form the free energy $f = E - TS$ of a N -unit polymer molecule, partially inside (n units) and partially

outside ($N - n$ units) of a nanotube, can be expressed as:

$$\begin{aligned}
f(n) &= f_1 + f_2 \\
&= k_B T \left[n \times \left(\frac{\Delta\mu}{k_B T} + \ln \frac{q_1}{q_2} \right) - (\xi_1 - 1) \ln (N - n) \right. \\
&\quad \left. - (\xi_2 - 1) \ln n \right] + \text{const.}
\end{aligned} \tag{1}$$

The suffixes 1 and 2 are for the portions of the polymer chain outside and inside of the nanotube, respectively, and we will use this notation throughout the paper. $\Delta\mu$ is the change in chemical potential per monomer between the two configurations. Whether there is an energy barrier for the insertion of a polymer into CNT, therefore, depends on the values of the parameters $\Delta\mu$, ξ , and q .

At finite temperature the translocation time describing how fast a molecule can be pulled into a CNT is a statistical value rather than a determinate one. The probability function $P(n, t)$, with n segments of the molecule into CNT at time t can be described by a one-variable Fokker-Planck equation, $\partial P(n, t)/\partial t = L_{FP}P(n, t)$. For cases with time-independent diffusion coefficients D , the operator $L_{FP} = \partial/\partial n [e^{-f/k_B T} (\partial/\partial n) D e^{f/k_B T}]$ [11]. Thus the mean translocation time τ , defined as $\int P(N, t) t dt$, for a N -unit polymer molecule into a CNT can be obtained by solving the above equation (assuming only the head unit of the polymer is inside the nanotube at $t = 0$) [4, 5, 11, 12]:

$$\begin{aligned}
\tau &= l_0^2 \int_1^{N-1} e^{f(n)/k_B T} dn \\
&\quad \int_1^n \frac{1}{D(n', N - n')} e^{-f(n')/k_B T} dn',
\end{aligned} \tag{2}$$

where l_0 is the length of a single monomer; $f(n)$ is the free energy as expressed in Eq. (1); $D(n, N - n)$ is the diffusion coefficient for a polymer molecule with $n/(N - n)$ units inside/outside the channel, with a general form:

$$\frac{1}{D(n, N - n)} = \frac{(N - n)^{\nu_1}}{D_1} + \frac{n^{\nu_2}}{D_2}, \tag{3}$$

where D_1 and D_2 are diffusion coefficients for a single monomer outside and inside CNT respectively, and ν_i is an exponential parameter, which has value of 0.5 in Zimm model where hydrodynamics interactions are taken into account, or 1 in Rouse model where hydrodynamics interactions are omitted [13], or 0 if only local friction at the end of the nanotube channel is considered. τ can be obtained by applying Eq. (1) and (3) into Eq. (2). For

cases of large N , an approximation for τ can be expressed as following, by calculating the integrals in Eq. (3) through integration by parts,

$$\tau = \frac{l_0^2}{|\frac{\Delta\mu}{k_B T} + \ln \frac{q_2}{q_1}|} \left[\frac{N^{\nu_1+1}}{(\nu_1+1)D_1} + \frac{N^{\nu_2+1}}{(\nu_2+1)D_2} \right] + O[(\xi_i - 1)N^{\nu_i}], \quad (4)$$

assuming that $N|\Delta\mu/k_B T| \gg 1$ and $\Delta\mu < 0$ (which is the case of interests here as will be discussed later). The second term in Eq. (4) can be omitted for large N ; and the diffusion parameters such as D_i and ν_i would dominate τ . To study the characteristic of D_i and ν_i , we use a system of polyethylene (PE) and CNT, because of the representative linear structure of PE and its simplicity.

A polymer molecule adsorbed into a nanotube is energetically favorable through gain in attractive potential energies due to van der Waals (VDW) interactions. We study the PE-CNT system using MD simulations. Tersoff-Brenner potentials [14] are used for carbon-carbon and hydrogen-carbon interactions, and the VDW potential between PE and CNT is modeled as a 6-12 type truncated Lennard Jones potential [15]. The VDW energy per monomer of a straight PE molecule is calculated as a function of distance from CNT walls in the radial direction, with axis of its backbone parallel to the axis of CNTs. The length of CNTs is chosen long enough as compared to that of PE to avoid edge effects. Shown in Fig. 1 are results for cases of CNT(10,10), (20,20) and (40,40). As it can be seen, PE molecules can be absorbed along the internal wall of CNTs, with the gain of VDW energy of up to 0.1eV/unit (on CNT(10,10)). The equilibrium distance of PE molecules from CNT walls is about 4Å. For small radius CNT such as (5,5) (not shown in Fig. 1), the adsorption is not favorable due to the repulsive interaction in VDW potential at small distance.

Although there is also a local energy minimum for PE molecules absorbed along the external walls of CNTs as seen from Fig. 1, it is energetically more favorable for the molecules to be absorbed inside than outside CNTs due to the curvature induced effects, and such effect decreases with an increase of the tube radii. The change in adsorption energies and barriers due to the registry of the molecules with CNT walls (moving along the CNT axis), are found to be negligible. More calculations show that the VDW energy is lower with the backbone structure of the PE molecules parallel to the CNT surface, compared to that with its backbone structure perpendicular to the surface. The difference is rather small ($\sim 0.001\text{eV}$); and the barrier separating the two local energy minimum is only 0.01eV,

small enough for PE molecules to switch freely between the two configurations at room temperature.

The energy gain through VDW potential per monomer gives a constant driving force $\mathbf{F} = -\nabla E$ for molecules to be pulled into CNTs and the translocation time for an isolated PE molecule to enter a CNT is estimated to be $t \sim N\sqrt{2m_0l_0/F}$ as according to Newton's law, where m_0 and l_0 are the mass and length of a single unit, respectively. For general cases of polymers and CNTs in aqueous solutions at finite temperatures, the thermodynamic effects need to be considered and can be included through MD simulations.

The insertion of PE molecules into a CNT is demonstrated using MD simulations and snapshots of such a process are shown in Fig. 2. PE molecules are surrounded by an aqueous decane ($\text{C}_{10}\text{H}_{22}$) solution outside CNTs, the influence of which on the dynamics of molecules is modeled through Langevin equation $m\dot{\mathbf{v}}(t) = -m\gamma\mathbf{v} + \mathbf{R}(t)$, with friction coefficient $\gamma = 50\text{ps}^{-1}$ [16]. The random force $\mathbf{R}(t)$ is assumed to be white noise, obeying the fluctuation-dissipation theorem with $T = 300\text{K}$. The wall of CNT is kept fixed. At $t = 0\text{ps}$, a 40-unit PE molecule is outside a CNT (10,10) (Fig. 2a); after $t = 500\text{ps}$, the molecule begins to enter the CNT due to the VDW interaction. The configurations of the molecule partially inside the CNT, and reaching the other end of the CNT are shown in Fig. 2(b) and (c), respectively. The side-views show that the PE molecule is curved around the CNT wall to minimize the VDW energy. Note that the time for the PE molecule to be pulled into the CNT, is a statistical value and Eq. (2) or Eq. (4) should be more suitable for its description. As we mentioned above, τ is directly related with diffusion of PE molecules inside CNTs, which is discussed below.

We study the diffusion of molecules inside CNTs also using MD simulations. As an example system, we choose a 40-unit PE molecule inside a CNT(10,10) channel. The CNT(10,10) is chosen because its diameter corresponds to the most commonly synthesized diameter of CNTs in experiments. The CNT is immersed in a heat bath controlled by Langevin friction force scheme [17]; and the PE molecule inside is not directly connected to the heat bath, but reaches its thermal equilibrium through the VDW interaction with CNT wall. The effect of energy transfers between molecules and CNT walls is taken into account in this way directly. The time step is 0.2fs and periodic boundary condition is used for the CNT (63\AA long). The heat bath is controlled at relatively high temperature $T = 600\text{K}$, to shorten the times for simulations. Simulations for room temperature are similar and the corresponding diffusion

coefficient D can be obtained easily as $D \sim T$.

PE molecules inside the CNT channels are found to be in extended configuration (with end-to-end distance $R_d \sim 28\text{\AA}$) as compared to the case in free space ($R_d \sim 18\text{\AA}$ [18]). This suggests a decrease of the effective coordination number for the inserted molecules. Similar MD simulations on PE molecules with 10 and 20 monomers show that $R_d \sim N$, rather than \sqrt{N} in free space. This is in agreement with prediction from the scaling theory for polymers in confined space [10]. The monomers in the PE molecules are found to be mostly distributed around 4\AA away from the CNT walls, which is the distance of VDW energy minimum. The distribution of the kinetic energy E_{kin} of the center mass (CM) of PE molecules is found to obey the Maxwellian distribution $e^{-E_{kin}/k_B T}$.

The self-diffusion coefficient D_{\parallel} of the CM of PE molecules along the CNT axis is related with the mean-squared displacement (MSD) function as following:

$$D_{\parallel} = \lim_{t \rightarrow \infty} \frac{1}{2t} \langle [r_{\parallel}(t + t_0) - r_{\parallel}(t_0)]^2 \rangle, \quad (5)$$

where $r_{\parallel}(t + t_0)$ is the coordinate of the CM of molecules along CNT axis direction. Shown in Fig. 3 is the MSD of PE molecules as a function of time in log-log scale at $T = 600\text{K}$. The MSD is averaged from 12 independent simulation trajectories and also averaged over initial times. In the beginning time at $0 < t < 30\text{ps}$, the collisions between molecules and CNT walls haven't reduced the ballistic transport feature, with the slope of $\log(\text{MSD})$ to $\log t \sim 2$; for longer time $t > 40\text{ps}$, the diffusion characteristics begin to show, with the slope of $\log(\text{MSD})$ to $\log t \sim 1$, which is the behavior described by Eq. (5). The ballistic transport could be important for a very short CNT channel. For the 40-unit PE molecule studied here, a critical length of CNTs ($\sim \bar{v}_{CM} \cdot t_c$), separating the two ranges, is estimated to be 35\AA , where \bar{v}_{CM} is mean velocity of CM of the PE molecule at $T = 600\text{K}$ and $t_c \sim 40\text{ps}$. The velocity auto-correlation function $C_{vv}(t)$, shown in the inset of Fig. 3, confirms that the correlations decrease with time and the critical time for $C_{vv}(t)$ approaching to zero is about 40ps . During the diffusion process, PE molecules mostly move along the CNT walls with a separation corresponding to the VDW energy minimum.

The diffusion coefficient D_{\parallel} of a 40-unit PE molecule inside CNT (10, 10) is found to be $25.4 \pm 0.5\text{\AA}^2/\text{ps}$ at $T = 600\text{K}$, using Eq. (5) with MSD data in time interval of $[60\text{ps}, 160\text{ps}]$. According to the reptation theory of a straight tube model for polymers [19], $D_{\parallel} \sim N^{-1}$. A

modified Einstein relation for a N -unit polymer can be written as,

$$D_{\parallel} = \frac{k_B T}{N m_0 \gamma_{eff}} \quad (6)$$

where m_0 is the mass of a monomer and γ_{eff} is the effective friction coefficient for a monomer. For a PE molecule, γ_{eff} is estimated to be $3.5 \times 10^{-2} \text{ps}^{-1}$ from Eq. (6). An estimation of D_{\parallel} for CH_4 ($N = 1$) gas molecules is found to be about $10^3 \text{\AA}^2/\text{ps}$ ($10^{-1} \text{cm}^2/\text{s}$) at $T = 300\text{K}$; it shows the faster diffusion of methane in CNTs compared with in zeolite such as silicalite ($D \sim 10^{-4} \text{cm}^2/\text{s}$) [8], although the above estimated value is smaller than that from the direct simulation of methane at zero pressure ($D \sim 10^0 \text{cm}^2/\text{s}$) [8]. The difference could be attributed to the energy transfers with CNT walls which was not considered in the direct simulation of methane; or also to possible corrections to Eq. (6) for its application in the cases of very small N , where the confinement effect is smaller compared with cases of longer molecules. The faster diffusion feature is expected to remain for long chain polymer in CNTs, compared with in ordinary zeolite channels, considering the same dependence of D on N as expressed in Eq. (6).

The Eq. (6) suggests that $\nu_2 = 1$ in Eq. (3); thus the translocation time expressed in Eq. (4) has N^2 dependence from the contribution of diffusion inside CNT. This feature is expected for other types of polymers too as it arises from the confinement of nanotube. For diffusion outside CNT, the Zimm model is suitable for cases of aqueous solutions, where $\nu_1 \sim 0.5$, leading to a $N^{1.5}$ dependence. For large N , the contribution from diffusion inside CNT dominates and an approximation for Eq. (4) is:

$$\tau \approx \frac{l_0^2}{\left| \frac{\Delta\mu}{k_B T} + \ln \frac{q_1}{q_2} \right|} \frac{N^2}{3D_2} \quad (N \gg 1) \quad (7)$$

The change in chemical potential $\Delta\mu$ is dependent on the relative structures and sizes of polymer and CNT systems, and properties of surrounding solutions. For a system of a PE molecule in its own solution, the VDW energy is about 0.05 eV/unit [18], thus a negative change of $\Delta\mu = -0.1 \text{ eV} + 0.05 \text{ eV} = -0.05 \text{ eV}$ is found, as the gain of VDW energies into CNT is up to 0.1 eV/unit . For long chain PE molecules, condition $N|\Delta\mu/k_B T| \gg 1$ for Eq. (4) and (7) is satisfied at room temperature. Thus τ is estimated as $N^2 \times 10^{-4} \text{ps}$ (taking $l_0 \sim 1 \text{\AA}$, $|\Delta\mu/k_B T| \sim 2$, $\ln(q_1/q_2) \sim 1$, and $D_2 \sim 10^3 \text{\AA}^2/\text{ps}$) at $T = 300\text{K}$. For a $N \sim 10^5$ long PE molecule, a fast translocation is found with $\tau \sim 1 \mu\text{s}$.

Other interactions, beside VDW potential, such as external electric fields in experiments of DNA through nanopores, can also bring changes to the chemical potential. In some

polymer/CNT systems there could be strong chemical bonding rather than the weak VDW potential. The translocation and diffusion properties in these systems could be different from studies present here.

In summary we have studied the translocation and diffusion of long chain polymer molecules through and inside CNT channels. The expression for translocation time τ is obtained from Fokker-Planck equation, which is found to be dependent on the chemical potential, entropy, and diffusion. For long N -unit polymers, the τ scales as N^2 . Calculations of VDW potential of polyethylene (PE) molecules show that the absorption of PE molecules on the internal walls of CNT is energetically favorable, with absorption energy up to 0.1 eV/unit. The diffusion coefficient calculated from mean-square displacement in MD simulations suggests very fast diffusion of polymer molecules inside CNT. The corresponding translocation time is estimated to be $\sim 1\mu\text{s}$ for a 10^5 -unit PE molecule.

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FIG. 1: The absorption energy (VDW) per monomer of a polyethylene molecule as a function of distance from CNT walls in radial direction. The axis of the backbone of the PE molecule is parallel to the axis of CNTs. The left side is for the internal of CNTs; and the right side is for the external of CNTs. The two sides are separated by CNT walls. Solid, dashed, and dotted lines are for CNT(10,10), (20,20) and (40,40) respectively.

FIG. 2: The snapshots of a 40-unit PE molecule into CNT (10,10) (15 Å) from MD simulations (see text for details). (a) $t = 0$ ps, the PE molecule is just outside the CNT; (b) $t = 600$ ps, the molecule is partially inside the CNT; (c) $t = 750$ ps, the molecule reaches the other end of the CNT.

FIG. 3: The mean-squared displacement (MSD) of the CM of polyethylene molecules inside CNT channel as a function of MD simulation time in log-log scale. The data is averaged from 12 independent simulation trajectories and also averaged over initial times. At beginning time ($0\text{ps} < t < 30\text{ps}$), the slope of $\log(\text{MSD})$ to $\log t \sim 2$, representing ballistic feature; at longer time ($t > 40\text{ps}$), the slope ~ 1 , representing diffusion feature. Insert: The velocity auto-correlation function (C_{vv}) as a function of MD simulation time.





